Environmental friendly and Durable Oil and water repellence finish on Technical Textiles

Reporting

Project Information

**TEX-SHIELD**

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**Coordinated by**
NORTH WEST TEXTILES NETWORK LIMITED

**United Kingdom**

Final Report Summary - TEX-SHIELD (Environmental friendly and Durable Oil and water repellence finish on Technical Textiles)

Executive Summary:
For many years, numerous well-known brands of performance textiles have been coated with perfluorocarbon chemistry to impart highly durable oil and water repellent (DWR) properties to the textile. In the early stages of the technology, repellency was provided by simple paraffin or wax coatings, which washed out over time. Following on from this, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are chemicals belonging to the family of perfluorochemicals (PFCs) and were developed into
products which became known as 'C8 chemistry'. Although PFC-C8 are used together with binders that act as glue to stick to the surface of fabrics, these are not chemically bonded to the substrate and can therefore leach out, potentially causing an environmental and/or ecological threat. In response to this, in January 2006, the U.S. Environmental Protection Agency (EPA) approached the eight largest fluorocarbon producers and requested their participation in the 2010/15 PFOA Stewardship Program, and their commitment to reduce PFOA and related chemicals globally in both facility emissions and product content by 95 percent by 2010, and 100 percent by 2015. Additionally, PFOS was added to Annex B of the Stockholm Convention on Persistent Organic Pollutants in May 2009. In response to these measures, the industry has developed perfluorohexanoic acid (PFHA), also known as ‘C6 chemistry’. Although claimed to be less harmful than PFOS, it is also less attractive to the end user both in effectiveness (i.e. how well the finished article repels water and/or oil) and durability (i.e. how long the repellent effect lasts after wearing and washing).

This leaves the textile and clothing supply chain, and its end users, with a problem: how to maintain established levels of performance in so-called DWR products whilst eliminating the undesirable C8 chemistry which is largely responsible for delivering the desired performance. The TEX-Shield project aimed to investigate potential solutions to this problem.

During the early months of the project, the partners elected to investigate three categories of potential solution that would benefit not only the SMEs and SME-AGs involved in the project, but also the wider textile and clothing supply chain. These categories were:
1) ‘Shorter chain’ PFC products with a view to identifying formulation and deposition parameters to yield optimum performance
2) Silicone/fluorosilicone approaches to reduce fluorine content whilst maintaining functional performance
3) Development of nano-structured fluorine free materials

The full report for the TEX-Shield project contains an expanded discussion of the results of each of these approaches. Although the ultimate goal of a PFC-free Durable Water Repellent treatment for textiles is yet to be attained, the deeper understanding of the complexities of the subject obtained and the advances made during the TEX-Shield project has brought that day closer.

Project Context and Objectives:
Durable Water and/or Oil Repellent treatments on textiles work by reducing the tendency of liquids to spread out and penetrate the fibres on contact with the substrate: instead, the liquid maintains a high ‘contact angle’ with the substrate. The repellency finish allows liquids to bead up and roll off the fabric, or liquid spills to be easily wiped away with a clean cloth. Thus, their usefulness in, for example, keeping skiers dry in heavy snowfall, or soft furnishings serviceable after food or drink spillages, is a highly desirable added-value attribute for the finished article.

The current fluoropolymer-based stain repellent treatments are known to pose significant health concerns. PFCs are either produced by electro fluorination or teleromerisation, manufacturing processes which give out unintended by-products of perfluorooctane sulphonates (PFOS) and perfluorooctanoic acid (PFOA). PFOA has the molecular formula C8F15O2H while PFOS is C8HF17O3S.
During service life, the PFC treatment is gradually leached from the fabric, and decomposes to PFOA and PFOS. Both PFOA and PFOS are very stable in the environment and, hence, are a significant ecological threat, as the levels reached in higher organisms (including people) can become significant. Consequently, the U.S. Environmental Protection Agency (EPA) and some of the biggest fluoropolymer manufacturers have cooperated in studies and have collected and shared their findings. The following results have been highlighted from this research about PFOA and PFOS:

- They are very stable in the environment, so they do not readily degrade.
- Once they enter the human body they are eliminated very slowly. This means that they remain in the body for relatively long periods of time: the half-life in humans is about 4.5 years.
- They cause adverse effects in laboratory animals that have been given high doses over a long period of time.

To put the project into economic context, the European Commission identified Personal Protective Equipment (PPE) as a ‘lead market’ (defined as a market which presents ‘a significant potential for global market leadership by European companies based on important scientific and technological developments achieved by European researchers’). Also, the annual sales value of the Outerwear market in the EU was estimated to be over €10 billion in 2012 (source: European Outdoor Group ‘State of Trade’ report http://tinyurl.com/jox6ntu ). Of this figure, 42% was defined as ‘outerwear top’ and a further 12% as ‘outerwear bottom’ garments. It is likely that a substantial percentage of these sales are for DWR products, which reinforces the importance of finding a suitable alternative to C8 chemistry. There is also significant demand for water and oil repellent garments (particularly in the PPE trade, which had a worldwide wholesale value of US$9.92 billion in 2014) and in soft furnishings (especially in the hotel trade), both of which have historically relied heavily on C8 chemistry to impart desirable characteristics to the finished product.

It can be readily seen that there is significant market demand for the DWR family of products, and the TEX-Shield partnership is well placed to exploit any new technology developed by the project, consisting as it does of end users (Eva Commerce and Panaz), and SME-AGs with outdoor wear, PPE and contract furnishings businesses amongst their membership.

In addition to the global details given above, a survey of SMEs throughout Europe was undertaken by the project team to provide guidance on the requirements placed on new repellent coatings from an industrial perspective. In summary, the respondents were clear that they required high performance repellency for water and oil, but, surprisingly, retention for 5-10 washes was seen as adequate, with little requirement for considerably higher durability.

The key objectives of the project were to investigate means of:
1) Eliminating problems with C8 PFCs’ by-products associated with textile treatments.
2) Providing a cost-effective alternative treatment which allows textiles to be provided with durable anti-soiling/anti-staining characteristics.
3) Reducing the total fluorine content in the treatment by means of new sol-gel derived additives in the form of nanoparticles or inorganic-organic hybrid networks.
4) Demonstrating performance on a representative scale, with regards to key technical parameters.
including soil resistance, abrasion resistance, cleaning cycle resistance.
5) Creating additional advantageous functions such as anti-static and anti-microbial characteristics to improve stability against mechanical, chemical impacts.
6) Developing flexible and versatile solutions for a broad range of textile supports different in structure (woven, knitted) and basic fibres (natural, synthetic or mixtures).
7) Developing a solution with a low ecological footprint, based on REACH-proof chemicals and taking into account safety and health issues.
8) Providing a full Life Cycle Analysis (including washability cycle) and assessment of techno-economic benefits, via benchmarking against current products.
9) Providing the necessary technological transfer and training via SME associations to ensure awareness and take up throughout the EC.

Project Results:
Our work gave us a unique understanding of candidate alternative methods to confer water and oil repellency to textile fabrics. This led us to conclude that, in the short to medium term at least, industry standard replacement of PFC-C8 chemistry is most likely to come from shorter chain PFCs – either PFC-C4 or, most probably, PFC-C6. Whether these alternatives will be acceptable in terms of environmental legislation remains to be seen. The German chemistry business Rudolf Chemie claimed in an issue of the magazine Textile Insights (February 2009) that “C6 is closest chemically to C8, but it contains no PFOA. It breaks down in the environment.”

Investigations into fluorine-free approaches led us to believe that the required standards of oil and soil repellence cannot be attained via non-fluorinated chemistries: some fluorine is likely to be required to produce an acceptable performance. On this basis hybrid systems such as fluoro-silicones may well offer promise as ‘composite approaches’, containing reduced fluorine content but offering high water repellence with good handle and durability.

Nanotechnology is another option: this appears to be a promising approach and the industry has developed innovative methods to deliver the required performance. However, the long-term effect of this technology on the environment is not clearly understood.

The coatings that have been developed and evaluated through this programme were intended to replace the incumbent materials but designed in such a way that the environment would be more tolerant toward them. To achieve this three approaches were followed:

1) Fluorocarbons with carbon chains smaller than eight.
2) A polysiloxane loaded with silica nanoparticles.
3) A completely fluorine-free nano-silica functionalised to provide repellency whilst binding to textile fibre surfaces.

Of these, Approach 1 can be considered as being closest to market as it was exploring the use of commercially available materials, such as C6 PFC. However it was established during this project that these shorter chained PFCs do not give comparable performance to the C8 PFCs. This implies that either the applications will have to accept a reduction in properties or the coatings will have to be boosted in some manner. This approach does offer a reduction in the perfluorocarbon content on fabrics and
garments and reduces the environmental impact. The approach of a direct replacement of C8 by C6 perfluorocarbons also would fit with existing processes currently used in the textile industry. This means that energy and waste expenditure would be similar to current systems but with a reduction in the environmental impact caused by the C8 fluorocarbons.

The second approach again uses commercially available materials although the specific materials are not currently used within the textile industry. These were siloxane polymers and silica nanoparticles that when combined were able to be applied and cured onto textile. These materials are fluorine-free and therefore fundamentally more environmentally friendly than the incumbent products. They were found to provide water repellency, which for some applications would be suitable for use in the textile industry.

However, the repellency to oil (oleophobicity) was not as good as the incumbent C8 perfluorocarbons. During the course of the project, attempts were made to improve the oil repellency, but that required the development of a novel post treatment that required a high temperature process and was also fluorine based, although smaller than the C8 fluorocarbons. It should also be stated that despite the post treatment, the level of oleophobicity was not still not comparable to the C8 PFC materials and so would require further development work before commercial trials were possible.

Using surface energy and contact angle measurements on model materials, the third approach demonstrated that by using functionalised nano-silica it should be possible to obtain a coating that had superhydrophobic and oleophobic properties without any fluorine content. This approach is still at the lower technology readiness levels and requires further product development before it could be considered for market evaluation.

The information gathered and subsequent calculations undertaken during the project show that the environmental impact of the materials in development will reduce the fluorine content of fabrics, with several approaches completely removing fluorine from the systems. With the exception of the UV cure process, all of the approaches discussed have been designed to fit with existing practices within the textile industry. The environmental impact of processing of these materials is mainly governed by the curing processes rather than the components or manufacture of the coatings themselves. The curing process can be improved in a number of ways, for instance by increasing packing efficiency as material is pushed through the ovens, or improving the efficiency of the oven, reducing cure times and temperatures, but these are outside the scope of this project, although the cure time is in some ways begun to be addressed with the UV cure system.

Although the ultimate goal of a PFC-free Durable Water Repellent treatment for textiles is yet to be attained, a number of promising routes have been explored and represent valuable progress towards the goal of reducing fluorine in coatings that would be suitable for technical textiles whilst still retaining the desired repellency performance. This has included materials and processes which can be implemented immediately such as the C6 chemistries boosted with paraffin wax or cyclodextrins.

Cyclodextrins were also shown to boost the performance of C4 PFCs. The sol gel system of Nano-X, boosted with paraffin wax also performed well, although the inference from some characterisation
performed on this system suggests that the Nano-X materials may not actually be sol gel. This is surprising and further work will be required to verify this.

The application of very thin coatings of C6 PFCs by plasma was also thoroughly explored and holds promise for some applications, especially where repeated washings are not a requirement.

A water-borne UV curable system has been developed using commercially available materials, which showed good repellency to both oil and water. Durability was further enhanced by the addition of a commercial fixative.

A filled polysiloxane, again based on commercially available ingredients was developed. This was found to be superhydrophobic, demonstrating self-cleaning behaviour. This material could be made at scale, through toll manufacture, relatively quickly. Attempts to improve the oil repellence of this material led to the development of synthesis routes to novel structures. Further work on these is required before they could be taken forward.

It has also been demonstrated that it is possible to achieve the hydrophobicity using a completely fluorine free system. This was achieved using novel silica nano-particles which have controlled levels of multiple functionalisations.

It should be noted here that, whilst concepts have been demonstrated, further work is required to take the materials to higher TRLs.

At the time of writing this report, the TEX-Shield project consortium has no applications for patents, trademarks or registered designs. One of major chemical companies in the world (Huntsman) has contacted the co-ordinator with a view to arranging a conference call to discuss the results of the TEX-Shield project in February 2016.

Potential Impact:
IMPACT ON EU SOCIETY
There are a number of benefits to the EU that will result from the successful development of PFC free (or reduced PFC) DWR treatments for textiles:

1) PUBLIC HEALTH BENEFITS - The existing PFC based chemicals – particularly C8 products - have been identified as a threat to human health. C8 PFCs have been found in the tissues, blood and foetal-cord of animals and humans. PFCs have been found to be persistent, bio-accumulative and toxic to mammalian species and also prone to cause certain cancers in laboratory test animals and are referred to as a ‘likely carcinogen’. C6 and C4 chemistry have yet to be subjected to the intense levels of scrutiny that C8 products have been, but there is a widely held belief that reducing the use of PFCs is a desirable objective.

2) INDIVIDUAL HEALTH BENEFITS – It has long been established that suitable PPE can help to not only reduce industrial accidents but also reduce absenteeism from less traumatic events such as the common cold. Thus, an effective DWR solution will help to reduce absenteeism in the workplace.

3) CONTRIBUTION TO REGULATORY FRAMEWORK - By providing a greater understanding of the science involved in DWR products, TEX-Shield has contributed to the elimination of hazardous chemicals detrimental to the environment and to cutting down the release of such substances into the environment. This will contribute to the EC Regulation 1907/2006 (REACH) that emphasizes on the safe use and
disposal of chemicals and chemical substances.

IMPACT ON TEXTILE SUPPLY CHAIN COMPETITIVENESS
The EU has identified Personal Protective Equipment (PPE) as a ‘lead market’, which offers ‘significant potential for global market leadership by European companies based on important scientific and technological developments achieved by European researchers’. In addition to this clear advantage, Outerwear is a > €10 billion per annum sector in the EU. Many of these products derive added value from DWR finishes, and the opportunity for European producers to gain market advantage by having access to ground-breaking technology is significant.

IMPACT ON PARTICIPANTS
The most evident potential benefit for the participants in TEX-Shield is in the ability to access a large market with an innovative, highly desirable product. The advantage of this has been identified by the widely respected academic Robert G. Cooper, who says in his book Winning at New Products “One of the top success factors we uncovered is delivering a differentiated product with unique customer benefits and superior value for the user.”

With annual worldwide workwear sales approaching $10 billion per annum, EU Outer Wear sales at €10 billion and an estimated 17.5 million hotel rooms worldwide in 2012 (source: STR Global), the market for DWR products is huge. Although no reliable figures exist for what proportion of these end uses involve DWR products, the absolute numbers are clearly substantial.

DISSEMINATION
INTERNAL - This includes all the actions aiming at ensuring a good diffusion of information and documentation among the project partners in order to increase the awareness. Internal dissemination has been achieved through the following channels:
• Private project website: the private website was set up and used to ensure for all the partners access to proper information and project progress. It was used as a database and collection for all the reports generated by each work package team as well as general project information, including all the presentations and seminars released by the Project Technical Committee and Project Management Boards.
• Internal meetings and workshops: Two types of internal meetings and workshops were used in the development of the project: conference calls and face-to-face meetings. As stated in the Consortium Agreement document, the regular meetings were the ones for the Project Steering Board (PSB), face to face, one every semester and the ones for the consortium conferences calls, organized quarterly. Industrial partners worked on the dissemination and use activities by involving their internal product groups and R&D teams.

EXTERNAL - External dissemination included actions aiming at ensuring the visibility and awareness of the project and the results outside the Consortium. These actions were concentrated on the scientific and SME community. The focus on SMEs was primarily delivered by the SME-AG partners. A number of other ‘routes to market’ were also employed, including
• Public project website, the TEX-Shield public web (http://www.texshield-project.eu) presents to the general public the objectives of the work, the organization, the partners composition, the internal and
external events, and the scientific publications.

- Promotional flyers
- Posters
- Workshops organized by the 4 SME Associations
- Promotional video (at the time of writing, this is being reviewed by the partners and will be uploaded to YouTube in early February 2016)

In total, TEX-Shield was promoted on over 80 separately identified occasions throughout the project lifetime. Some notable dissemination events and approximate number of attendees were as follows:

- Poster presentation, ‘Mood’ fair, Brussels, September 2013, 10,000 attendees
- Poster presentation, ‘Techtextil’ trade fair, Frankfurt June 2013, estimated 27,500 attendees
- Workshop, student exchange event, Ghent December 2013, 31 attendees
- Leaflet distribution, Euratex conference, Brussels March 2014, 240 attendees
- Scientific lecture by INSA Lyon, Berlin August 2014, 600 attendees
- Lecture, EnviroNord, Lille June 2015, 70 attendees
- Display stand, TWI open day, Cambridge October 2015, 90 attendees

List of Websites:

http://www.texshield-project.eu/  

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